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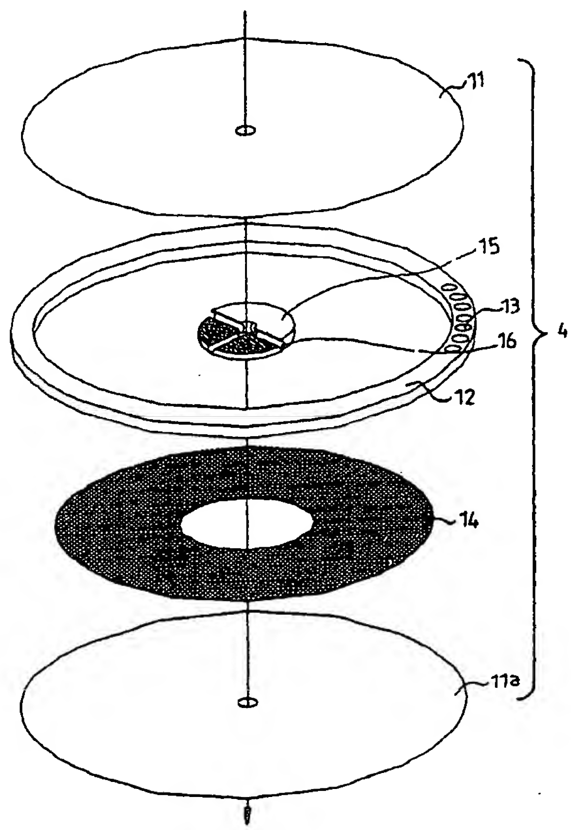
(54) Title: MINIATURE FUEL REFORMER AND SYSTEM USING METAL THIN FILM

(57) Abstract

Disclosed herein is a miniature fuel reformer for use in a fuel cell driven vehicle using a metal thin film. The reformer comprises a plurality of unit modules connected together in series, in parallel, or in a combination thereof. Each of the unit modules includes an inner housing having a cylindrical shape while having top and bottom walls, an outer housing arranged around the inner housing while being radially spaced from the inner housing, a hydrogen separation reaction chamber defined in the inner housing, a combustion catalyst chamber defined between the inner and outer housings, a fuel inlet provided at the top wall of the inner housing, a plurality of vertically spaced hydrogen gas separation cells arranged in the hydrogen separation reaction chamber, a steam reforming catalyst filled in the hydrogen separation reaction chamber between adjacent ones of the hydrogen gas separating cells, a plurality of vertically spaced cylindrical support members centrally arranged in the hydrogen separation reaction chamber while defining a hydrogen passage communicating with the hydrogen separation cells, a permeate discharge tube coupled to the bottom wall of the inner housing, a plurality of raffinate outlets provided at the bottom wall of the inner housing, and a plurality of combustion fuel/air inlets respectively connected to the raffinate outlets by conduits.



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MINIATURE FUEL REFORMER AND SYSTEM USING METAL THIN FILM

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates in general to a fuel reformer utilizing a metal thin film for use in a fuel cell driven mobile vehicle which makes use of, as a fuel, alcohol such as methanol, ethanol, etc. More particularly, the invention relates to a miniature fuel reformer and a system thereof for use in a fuel cell driven mobile vehicle, which enables a reduction in the entire size by adopting an integrated hydrogen generation/separation type in which the steam reforming reaction for the hydrogen generation, and the separation reaction for the hydrogen separation are carried out simultaneously in the same reactor by the metal film property which selectively permeates only hydrogen of a reforming gas containing hydrogen, and by the principle by which the reaction rate increases beyond its- equilibrium limit.

Description of the Prior Art

In general, a fuel cell system by which the chemical energy converts directly to the electric energy with a chemical reaction between a hydrogen gas and an electrolyte, is used in the field in which no internal combustion engine is substantially utilized, such as in the case of spaceship. The fuel cell system is also used as a system for supplying electric power to an

electric driven mobile vehicle. In particular, in recent years, the importance of the fuel cell system is increasingly highlighted due to the tightening of restrictions on air pollution, and the limitation of the development of electric vehicles using battery power.

Moreover, with increasing interest in energy efficiency and the environmental pollution problem, it is accepted that internal engine driven vehicles can be virtually replaced with electric vehicles using fuel cells. However, there are various technically limiting factors that need still to be resolved, such that these fuel cell driven vehicles be widely commercially available. In particular, in a fuel cell driven vehicle that uses hydrogen gas as a fuel, all the problems with the construction of infrastructure for the storage, delivery, and supply of the hydrogen fuel act as limiting factors in virtually widely utilizing the fuel cell driven vehicle.

Thus, the development of a fuel reformer, wherein a liquid fuel such as methanol, ethanol, gasoline, and the like is reformed to generate hydrogen which is then separated for utilization as a fuel, has made recent progress. However, in order for such a fuel reformer to be widely utilized, developing a fuel reformer having smaller size, lighter weight, and excellent response to load is necessary. Particularly significant is that this fuel reformer is made smaller and lighter so that it can be mounted on the vehicle.

In addition, in recent fuel cell vehicles, there is used a Solid Polymer Electrolyte Fuel Cell(hereinafter, called "SPEFC"). Such a SPEFC, however, has a shortcoming

in that it loses easily its activity by virtue of CO contained in hydrogen gas, that is, the fuel. For this reason, it is significant to lower the concentration of CO to a minimum.

Furthermore, to develop a fuel cell vehicle using a liquid fuel, thereby resolving the above described problems with respect to the use of the hydrogen gas fuel, a process for preparation of hydrogen that utilizes the prior art steam reforming reaction is developed worldwide. However, this technology has a problem in decreasing the total size of the fuel reformer system, because the steam reforming reaction and the hydrogen separation reaction are carried out in different reactors as shown in FIG. 1.

For example, in US Patent No. 4,613,436, there is an effort to decrease the size of a hydrogen separation apparatus by arranging a plurality of vertically spaced circular hydrogen separation membranes while interposing airtight protrusions between adjacent ones of the membranes such that spaces each defined between adjacent membranes by the airtight protrusions are isolated from one another. Through each of the hydrogen separation membranes is passed the reforming gas flow to separate hydrogen which is then captured. However, the structure of this hydrogen separation apparatus is very unsuitable for mass production, and also has difficulty in maintaining the airtightness at fixed portions. To resolve these problems, US Patent No. 5,536,405 proposes inserting gaskets between the hydrogen separation membranes during the arrangement of the membranes such that the resultant apparatus may be suitable for mass

production and may also easily maintain the airtightness between the hydrogen separation membranes. A drawback with the apparatus in the latter patent, however, is that it is heavy in weight due to the application of the gasket means.

Meanwhile, an attempt to improve the performance of the fuel reformer was made. US Patent No. 5,458,857 attempted to carry out, in separate regions, the hydrogen gas generation process by the endothermic steam reforming of methane, and the exothermic transition reaction for transition of carbon monoxide and steam to carbon dioxide and hydrogen so as to improve the efficiency of the fuel reformer, thereby realizing the miniaturization of the fuel reformer. However, the problems associated with this patent are that the necessary heat cannot be supplied by only the heat from the transition reaction, and the structure of the fuel reformer used is complicated such that the efficiency is virtually lowered. Furthermore, US Patent No. 5,741,474 attempted to simultaneously practice, in a certain space, the partial oxidation of methane, as an exothermic reaction, and the reforming reaction, as an endothermic reaction, thereby maximizing the heat transfer efficiency. However, there is a drawback in that both reactions cannot be efficiently controlled, thereby to reduce the performance of the fuel reformer. Japanese Patent Application No. 93-147902 attempted to supply the necessary heat for the reaction by re-using, as a fuel, some of the hydrogen generated by the reaction of methanol with water, so as to improve the performance of the fuel reformer and to miniaturize the fuel reformer as well. However, there is a problem in

that a separate device is necessary for an initial heating, thereby limiting the miniaturization of the fuel reformer.

The above described inventions have limitations on the performance improvement and the miniaturization of the fuel reformer, because they attempted the performance improvement and the miniaturization by the improvement of the structure of the fuel reformer, without resolving the prior art problem in that the fuel reformer and the hydrogen separation apparatus must be separately present.

In an attempt to overcome such limitations, US Patent No.5,888,273 discloses a hydrogen generation device in which, after positioning a long tube-shaped membrane for separation of hydrogen and a steam reforming catalyst in the same space, hydrogen gas is separated, and some of the reforming gases, containing hydrogen, carbon monoxide, carbon dioxide, steam, etc. are transported to a separate location, and then are burned, thereby supplying the necessary heat for the reforming. However, such a device is problematic in that an initial ignition is difficult. Another problem is that the heat transfer efficiency of the device in supplying the necessary initial heat for the start of the reforming reaction, and heat for maintaining a necessary membrane temperature for the permeation of hydrogen, is poor. These problems are considered the significant drawbacks against the fast initial starting period and dynamic response of the fuel cell driven vehicle. In addition, because of the complicated structure and the use of the long tube-shaped hydrogen separation membrane, this

hydrogen generation device is unsuitable for a process, for example a manufacturing process of vehicles, for which mass production is required.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a miniature fuel reformer in which a metal thin film selectively permeating only hydrogen from a fuel is utilized to lower, to a very low degree, a concentration of carbon monoxide(CO) contained in the hydrogen fuel supplied to an anode of a SPEFC, thereby capable of reducing remarkably a poisoning of the anode by carbon monoxide.

It is other object of the present invention to provide a miniature fuel reformer in which unit modules are connected with each other in series, parallel, or a combination thereof, thereby capable of supplying, in a suitable way, a necessary amount of hydrogen to a vehicle.

It is another object of the present invention to provide a unit module in which a reaction for reforming of a liquid fuel and a reaction for separation of hydrogen are carried out in the same reactor as shown in FIG. 2, and therefore to provide a miniaturized fuel reforming system that can be easily mounted within the fuel cell driven vehicle.

To accomplish the above objects, the present invention provides a miniature fuel reformer for use in a fuel cell driven vehicle comprising a plurality of unit modules connected with each other in series, parallel, or

a combination thereof, each of the unit modules including: an inner housing having a cylindrical shape while having top and bottom walls; an outer housing arranged around the inner housing while being radially spaced from the inner housing; a hydrogen separation reaction chamber defined in the inner housing;

a combustion catalyst chamber defined between the inner and outer housings and contained with a combustion catalyst for supplying heat needed in the inner housing;

a fuel inlet provided at the top wall of the inner housing and adapted to introduce liquid fuel into the hydrogen separation reaction chamber;

a plurality of vertically spaced hydrogen gas separation cells arranged in the hydrogen separation reaction chamber and adapted to selectively permeate hydrogen contained in the fuel introduced in the hydrogen separation reaction chamber, thereby separating the hydrogen from the fuel; a steam reforming catalyst filled in the hydrogen separation reaction chamber between adjacent ones of the hydrogen gas separation cells and adapted to reform the fuel introduced in the hydrogen separation reaction chamber; a plurality of vertically spaced cylindrical support members centrally arranged in the hydrogen separation reaction chamber while defining a hydrogen passage communicating with the hydrogen gas separation cells, thereby allowing the hydrogen separated from the fuel to be discharged from the hydrogen gas separation cells, each of the cylindrical support members being interposed between adjacent ones of the hydrogen gas separation cells and serving to regulate a gap defined between the adjacent hydrogen gas separation

cells; a permeate discharge tube coupled to the bottom wall of the inner housing, the permeate discharge tube communicating with the hydrogen passage defined by the cylindrical support members to allow the hydrogen introduced in the hydrogen passage to be outwardly discharged from the hydrogen passage; a plurality of raffinate outlets provided at the bottom wall of the inner housing and adapted to discharge a portion of the fuel, not permeating any one of the hydrogen gas separation cells, from the hydrogen separation reaction chamber; and a plurality of combustion fuel/air inlets respectively connected to the raffinate outlets by conduits and adapted to introduce the fuel portion discharged from the raffinate outlets into the combustion catalyst chamber, along with air, so that the fuel portion is burned in the combustion catalyst chamber.

Moreover, the present invention provides a miniature fuel reforming system for use in fuel cell driven vehicles, comprising: a fuel preheater for preheating and vaporizing a liquid fuel; a fuel reformer for receiving the vaporized fuel via a fuel supply header and separating hydrogen from the received fuel to produce a reforming gas, the fuel reformer having a hydrogen separation reaction chamber for separating hydrogen from the received fuel, and a combustion catalyst chamber containing a combustion catalyst for supplying heat needed in the hydrogen separation reaction chamber, the combustion catalyst chamber receiving the hydrogen-separated fuel, that is, a raffinate; means for receiving a permeate, that is, the hydrogen separated by and discharged from the hydrogen separation reaction chamber

of the fuel reformer, via a permeate header, controlling the pressure of the received permeate, and supplying the pressure-controlled permeate to an anode of a fuel cell; means for controlling the pressure of the raffinate discharged from the hydrogen separation reaction chamber, thereby controlling the hydrogen separation reaction chamber of the fuel reformer; and valve means for supplying the raffinate to the combustion catalyst chamber of the fuel reformer.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects, features and advantages of the invention will be apparent to those skilled in the art to which the present invention relates from reading the following specification with reference to the accompanying drawings, in which:

FIG. 1 is a block diagram schematically showing that the steam reforming reaction and the hydrogen separation reaction are separately carried out with the prior art fuel reforming system.

FIG. 2 is a block diagram schematically showing that the steam reforming reaction and the hydrogen separation reaction are carried out in the same reactor with a fuel reformer according to the present invention.

FIG. 3 is a schematic view of the construction of a unit module of a fuel reformer according to the invention.

FIG. 4 is a schematic view of a construction of a hydrogen gas separation cell according to the invention, that permeates hydrogen from a reformed gas containing

hydrogen.

FIG. 5 and FIG. 6 each is a schematic view showing passages for a fuel for the steam reforming, and for a permeate that is hydrogen permeated through the hydrogen gas separation cell, and also for a raffinate that is hydrogen non-permeated through the cell.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. 3 schematically shows the construction of a unit module 1 included in a miniature fuel reformer for a fuel cell driven vehicle according to the invention.

A plurality of the unit modules 1 are connected in series, parallel, or a combination thereof with each other, to constitute the fuel reformer of the invention. The unit module 1 has a fuel inlet 17 which is formed on its upper end and into which a liquid fuel, for example, alcohol such as methanol, ethanol, etc., is introduced. Moreover, the unit module 1 has a hydrogen separation reaction chamber 7. In the hydrogen separation reaction chamber 7, a steam reforming catalyst 3 is contained which serves to reform the fuel introduced through the fuel inlet 17. The hydrogen separation reaction chamber 7 also contains therein a plurality of vertically spaced hydrogen gas separation cells 4 for permeating and separating only hydrogen from the reforming gas. The hydrogen separation reaction chamber 7 is defined in an inner housing 8 having a cylindrical shape while having top and bottom walls. Between adjacent ones of the hydrogen gas separation cells 4, there is interposed a plurality of vertically spaced cylindrical support

members 6 fixed to those cells 4 at both ends thereof in accordance with a diffusion welding process. These cylindrical support members 6 are centrally arranged in the hydrogen separation chamber 7 while defining a hydrogen passage communicating with the hydrogen separation cells 4, thereby allowing the hydrogen separated from the fuel to be discharged from the hydrogen gas separation cells 4. The cylindrical support members 6 also serve to control a gap defined between the adjacent cells 4.

A combustion catalyst chamber 9 is arranged around the inner housing 8. The combustion catalyst chamber 9 has a combustion catalyst 5 for transferring the necessary heat to the hydrogen separation reaction chamber 7. This combustion catalyst chamber 9 is defined between the inner housing 8 and an outer housing 10 arranged around the inner housing 8.

A permeate discharge tube 25 is coupled to the bottom wall 1 of the inner housing 8. This permeate discharge tube 25 is also communicated with the hydrogen passage defined by the cylindrical support members 6 to allow the hydrogen introduced into the hydrogen passage to be outwardly discharged from the hydrogen passage. Meanwhile, in order for a raffinate, that is, a reforming gas non-permeated through the hydrogen gas separation cells, to discharge from the hydrogen separation reaction chamber, a plurality of raffinate outlets 25 are formed at an inclined bottom wall of the inner housing 8. In addition, although not shown in FIG. 3, a plurality of combustion fuel/air inlets respectively connected to the raffinate outlets by conduits. These combustion fuel/air

inlets are adapted to introduce the fuel portion discharged from the raffinate outlets 25 into the combustion catalyst chamber 9, along with air, so that the fuel portion is burned in the combustion catalyst chamber 9.

Meanwhile, the hydrogen gas separation cells 4 each includes one or more channels 13 at its peripheral portion to allow the fuel to flow therethrough.

The construction of each of the hydrogen gas separation cells will now be described in detail with reference to FIG.4. Each hydrogen gas separation cell 4 comprises a pair of spaced metal films 11 and 11a adapted to selectively separate only hydrogen, and an annular support plate 12 made of copper or a copper alloy and provided at its peripheral portion with one or more vertical fuel channels 13. The support plate 12 is attached to the metal films 11 and 11a at opposite surfaces thereof, and therefore supports the metal thin film 11 and 11a. The hydrogen gas separation cell 4 also includes a support layer 14 (a porous separation membrane) serving to provide a passage for hydrogen permeated through the metal film 11 while maintaining a structural stability of the hydrogen gas separation cells 4. There is also a central support disk 15 made of copper or a copper alloy. The central support disk 15 is provided with a central hole denoted by no reference numeral and at least one radial hole 16. The radial hole 16 extends radially throughout the diameter of the central support disk 15 while communicating with the central hole formed at the central support disk 15 such a fashion that permeate, that is, hydrogen permeated

through the metal films 11 and 11a, passes therethrough. Also, the central hole is communicated with the hydrogen passage defined by the cylindrical support members 6.

Moreover, in order to prevent a degradation in the hydrogen separation performance of the steam reforming catalyst 3 by a direct contact of the steam reforming catalyst 3 with the metal film 11, a layer, which may be the support layer 14, is disposed between the steam reforming catalyst 3 and the metal film 11. Preferably, the support layer 14 is made of a porous separation membrane.

In such a hydrogen gas separation cell 4, hydrogen in the reforming gas generated by reforming the fuel with the steam reforming catalyst 3 is adsorbed onto an outer surface of the metal film 11 and separated from the fuel. The separated hydrogen atoms are permeated through the metal film 11 and then are bonded into hydrogen molecules at an inner surface of the metal film 11. The hydrogen molecules are passed through the radial hole and central hole formed at the central support disk 16 and then discharged from the hydrogen separation reaction chamber 7 through the permeate discharge tube 25.

In such a hydrogen selective-separation reaction, a higher pressure differential between the inner surface and the outer surface of the metal film 11, as well as a higher surface temperature, result in an increased permeation performance of the metal film 11. In addition, to keep the surface of the metal film 11 clean is necessary for better permeation performance of the metal film. The metal films 11 and 11a used in the invention includes the film made of palladium-based alloy, such as

Pd-Cu based alloy or Pd-Ag based alloy, and a metal film or metal foil made of vanadium(V), nickel(N) or an alloy thereof and coated with palladium.

Moreover, the steam reforming catalyst 3 useful in the invention includes a steam reforming catalyst based on Cu-Zn alloys, as well as a steam reforming catalyst containing precious metals in the amount of at least 0.01% by weight, such as Pt.

Furthermore, a hydrogen production capacity of the respective unit modules 1 in the fuel reformer can be varied freely depending on the surface area of the respective metal film 11, and the amount of the steam reforming catalyst 3 being filled. This allows the capacity of the modules to regulate freely. Namely, the amount of the steam reforming catalyst 3 filled can be varied depending on a height of the respective cylindrical support members 6, and a surface area of the metal film 11 can be varied with the diameter of the support plate 12. Accordingly, the hydrogen production capacity of the respective unit modules in the fuel reformer can be determined freely depending on the surface area of the respective metal film 11, and the amount of the steam reforming catalyst 3.

The support plate 12 supporting the metal films 11 and 11a, and the central support disk 15, are connected with each other by diffusion welding such that there is no gap between the inside and the outside of the respective hydrogen gas separation cells 4. Therefore, the concentration of other reforming gases poisonous to the fuel cell stack, particularly carbon monoxide, is very low, thereby maintaining the performance of the fuel

cell stack for a longer time.

As described above, it is preferable that the fuel channels 13 formed at the peripheral portion of the support plate 12 are arranged in a zig-zag as shown in FIG. 3, when connecting the respective hydrogen gas separation cells 4 with the cylindrical support members 6. This provides an increase in the contact efficiency between the fuel and the steam reforming catalyst 3, as well as an increase in the contact efficiency between the reforming gas and the metal film 11.

Referring to FIGS. 5 and 6, various passages and a reaction process will now be described below. In FIGS.5 and 6, arrows shown as solid lines depict a fuel passage 19, arrows shown as dotted lines depict a permeate passage 18, and arrows shown as one dot chain lines depict a raffinate passage 20.

A fuel, for example, alcohol such as methanol, ethanol, etc., that is pre-vaporized by a fuel preheater(not shown) disposed outside of the fuel reformer, is introduced into the hydrogen separation reaction chamber 7 through the fuel inlet 16 formed at the top wall of the inner housing 8. The introduced fuel is heated with combustion heat from the combustion catalyst chamber 9 to a temperature in the range of from 150°C to 600°C that is the temperature required by the hydrogen separation reaction chamber 7. The heated fuel flows downwardly to the hydrogen gas separation cells 4 through the fuel channels 13 formed at the peripheral portion of the support plate 12 of the respective cells 4, while contacting with the steam reforming catalyst 3 filled therebetween. The fuel contacted with the catalyst

3 is subjected to the reforming reaction as indicated in the following reaction scheme, to convert it into a reforming gas essentially consisting of hydrogen, carbon dioxide, and the remainder of water:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \qquad \Delta H_{298} = 130.99\ KJ$$

Such a reforming gas is then contacted with the metal film 11 that are connected to the support plate 12 by the diffusion welding. Only hydrogen of the fuel is selectively permeated through the metal films 11 and 11a, and is passed through the radial hole 16 formed at the central support disk 15, and then is discharged from the permeate discharge tube 25. Moreover, a raffinate that is a reformed gas non-permeated through the hydrogen gas separation cells 4 is discharged through raffinate outlets 26 formed along an inclined bottom wall of the inner housing 8, and is passed through conduits 29 and the combustion fuel/air inlets 21, and then introduced into the combustion catalyst chamber 9.

Meanwhile, the steam reforming reaction as indicated in the above reaction scheme is the endothermic reaction for which much heat is necessary. It is preferable that the necessary heat for such an endothermic steam reforming reaction is obtained by a heat exchange with the combustion heat. For such a heat exchange, methods may be used wherein a fuel stream supplied to the hydrogen separation chamber 7 and a fuel stream supplied to the combustion catalyst chamber 9 are the cocurrent flows, or wherein both streams are the countercurrent flows. However, the latter method is preferred for an

increase in heat efficiency by more effective heat exchange. Namely, in the raffinate being discharged from the hydrogen separation chamber 7 without permeating the hydrogen gas separation cells 4, there is contained hydrogen in the range of 1 to 70% by weight that varies depending on operation conditions of the hydrogen separation reaction chamber 7. Accordingly, where the raffinate is used as a fuel in the combustion catalyst chamber 9, there is no need for the supply of a separate fuel. This can further improve the energy efficiency of the fuel reformer.

The above described unit modules are connected with each other in series, parallel, or a combination thereof to constitute the fuel reformer that is a part of the fuel reforming system.

Hereinafter, the operation of the fuel reforming system using the fuel reformer of the invention will be described with reference to FIG. 7.

The fuel reforming system according the invention comprises a fuel preheater 22 for preheating a liquid fuel, such as methanol, etc., a fuel reformer 30 in which a plurality of unit modules 1 are connected with each other in series, parallel, or a combination thereof, and a pressure controller 24 for controlling pressure of a permeate, that is, hydrogen discharged the unit modules. The fuel reforming system also includes a raffinate pressure controller 23 for controlling a pressure of hydrogen separation reaction chamber 7 of the respective unit modules 1, a fuel supply header 28 for supplying the liquid fuel to the respective unit modules 1, a permeate header 27 for collecting a permeate discharged from the

hydrogen separation reaction chamber 7 of each unit module, and a valve 2 for supplying, to a combustion catalyst chamber of the respective unit modules, fuel non-permeated through metal thin films 11 in each unit module.

In such a fuel reforming system, the fuel, such as methanol, etc., is vaporized in the fuel preheater 22 comprising the fuel injector or the heat exchanger, and is passed to the fuel supply header 28. Thereafter, the fuel is passed through a fuel inlet 17 formed on the top wall of the inner housing arranged in the respective unit modules 1, and then introduced into the hydrogen separation reaction chamber 7 in which the fuel is subjected to the fuel reforming reaction and the hydrogen separation reaction simultaneously.

After the permeate generated by the above reactions is collected in the permeate header 27 again, it is supplied to an anode of the fuel cell stack. At this point, the pressure controlling device 24 composed of the compressor or the pressure controlling valve, etc. is disposed on the permeate header 27, such that, as occasion demands, the permeate pressure is controlled depending on the operating pressure of the fuel cell stack.

Moreover, the pressure of the hydrogen separation reaction chamber is controlled by the pressure controller, and the raffinate is passed through the pressure controller 23 to drop its pressure to an atmospheric pressure. Thereafter, the raffinate is passed to the valve 2. As occasion demands, the raffinate is passed from the valve 2 to the combustion catalyst

chamber 9 to be utilized as the fuel. This highly increases the energy efficiency of the fuel reformer.

Furthermore, when the heat exchanger is used as the fuel preheater 22, the heat supplied to the fuel preheater is heat-exchanged with a combustion gas discharged from the combustion catalyst chamber 9, to increase the energy efficiency.

Additionally, as described above, the fuel reformer 30 has a construction capable of controlling the hydrogen production rate, in that the unit modules are simply connected with each other in series, parallel, or a combination thereof depending on the necessary hydrogen amount for the fuel cell stack. Thus, the fuel reformer is suitable for mass production.

Even though the fuel reformer of the invention corresponds to the hydrogen generation and supply apparatus, this may be also applied in various fields including devices that require the hydrogen generation and the hydrogen purification from the mixed gases containing hydrogen, particularly the production of hydrogen of high purity.

In particular, the fuel reformer of the invention utilizes the palladium-based metal film of the property selectively separating only hydrogen from the fuel to reduce remarkably the concentration of CO in a hydrogen fuel supplied to an anode of SPEFC. This provides reduction in the poisoning of the anode by CO, and also enables the production of the proper amount of hydrogen from the respective unit modules. In addition, the fuel reformer is essentially composed of a plurality of the unit modules connected simply with each other in series,

parallel, or a combination thereof. The fuel reformer has a construction adapted for mass production, and therefore may supply various capacities of hydrogen required by the fuel cell driven vehicles.

When the inventive miniature fuel reformer using the metal thin film is applied to the fuel cell driven vehicle, the hydrogen production reaction(such as the steam reforming reaction) and the hydrogen separation reaction are carried out in the same reactor. As a result, the fuel reformer may supply, to an anode of the fuel cell, highly pure hydrogen having a remarkably low carbon monoxide concentration, without requiring a separate apparatus for hydrogen separation. This results in a decrease in poisoning of the anode by carbon monoxide. This also results in a remarkable decrease in size of the fuel reformer to allow the fuel reformer to easily mount in the vehicle. In addition to the above advantages, as the fuel reformer is fabricated with the unit module having certain hydrogen production capacity, to supply the varied amounts of hydrogen required by the fuel cell driven vehicle is possible with a simple module assembly only. This yields an efficient increase in the necessary assembly productivity for mass production.

Although the preferred embodiments of the invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

WHAT IS CLAIMED IS:

1. A miniature fuel reformer for use in a fuel cell driven vehicle comprising a plurality of unit modules connected with each other in series, parallel, or a combination thereof, each of the unit modules including:

an inner housing having a cylindrical shape while having top and bottom walls;

an outer housing arranged around the inner housing while being radially spaced from the inner housing;

a hydrogen separation reaction chamber defined in the inner housing;

a combustion catalyst chamber defined between the inner and outer housings and containing a combustion catalyst for supplying heat needed in the inner housing;

a fuel inlet provided at the top wall of the inner housing and adapted to introduce liquid fuel into the hydrogen separation reaction chamber;

a plurality of vertically spaced hydrogen gas separation cells arranged in the hydrogen separation reaction chamber and adapted to selectively permeate hydrogen contained in the fuel introduced in the hydrogen separation reaction chamber, thereby separating the hydrogen from the fuel;

a steam reforming catalyst filled in the hydrogen separation reaction chamber between adjacent ones of the hydrogen gas separating cells and adapted to reform the fuel introduced in the

hydrogen separation reaction chamber;

a plurality of vertically spaced cylindrical support members centrally arranged in the hydrogen separation reaction chamber while defining a hydrogen passage communicating with the hydrogen separating cells, thereby allowing the hydrogen separated from the fuel to be discharged from the hydrogen separation cells, each of the cylindrical support members being interposed between adjacent ones of the hydrogen gas separation cells and serving to regulate a gap defined between the adjacent hydrogen gas separation cells;

a permeate discharge tube coupled to the bottom wall of the inner housing, the permeate discharge tube communicating with the hydrogen passage defined by the cylindrical support members to allow the hydrogen introduced in the hydrogen passage to be outwardly discharged from the hydrogen passage;

a plurality of raffinate outlets provided at the bottom wall of the inner housing and adapted to discharge a portion of the fuel, not permeating through any one of the hydrogen gas separation cells, from the hydrogen separation reaction chamber; and

a plurality of combustion fuel/air inlets respectively connected to the raffinate outlets by conduits and adapted to introduce the fuel portion discharged from the raffinate outlets into the combustion catalyst chamber, along with air, so that the fuel portion is burned in the combustion catalyst chamber.

2. The miniature fuel reformer of claim 1 wherein each of the hydrogen gas separation cells comprises:

a pair of spaced metal films adapted to selectively separate hydrogen from the fuel;

an annular support plate interposed between the metal films and attached to the metal films at opposite surfaces thereof, the support plate having at least one fuel channel at a portion thereof;

a support layer interposed between the metal films inside the support plate and adapted to provide a structural stability for the metal films to withstand a high pressure, the support layer having a porous separation film structure to provide a passage for the hydrogen introduced into the interior of the hydrogen gas separation cell defined between the metal films; and

a central support disk arranged inside the support layer in such a fashion that it is vertically aligned with the cylindrical support members, the central support disk having at least one radial hole communicating with the hydrogen passage provided by the support layer and with the hydrogen passage defined by the cylindrical support members, thereby serving as a permeate passage.

3. The miniature fuel reformer of claim 1 wherein the steam reforming catalyst contains at least one metal component selected from the group consisting of Cu, Zn, Fe, Cr, Ti, and Ni, or contains at least one precious metal in the amount of at least 0.01% by weight based on the weight of the catalyst.

4. The miniature fuel reformer of claim 2 wherein

the respective metal films is made of a palladium-based alloy or a metal foil coated with palladium.

5. The miniature fuel reformer of claim 2 wherein the support plate and the metal films, and the central support disk and the metal films, respectively, are attached to each other by a diffusion welding.

6. The miniature fuel reformer of claim 2 wherein the hydrogen gas separation cells are arranged in the hydrogen separation reaction chamber such that the fuel channels are located in a zigzag, whereby a contact efficiency between the fuel and the steam reforming catalyst, and a contact efficiency between the reforming gas and the metal films are increased.

7. The miniature fuel reformer of claim 1 wherein the respective cylindrical support members is fixed to the hydrogen gas separation cells by a diffusion welding.

8. A miniature fuel reforming system for use in fuel cell driven vehicles, comprising:

a fuel preheater for preheating and vaporizing a liquid fuel; a fuel reformer for receiving the vaporized fuel via a fuel supply header and separating hydrogen from the received fuel to produce a reforming gas, the fuel reformer having a hydrogen separation reaction chamber for separating hydrogen from the received fuel, and a combustion catalyst chamber contained with a combustion catalyst for supplying heat needed in the hydrogen separation reaction chamber, the

combustion catalyst chamber receiving the hydrogen-separated fuel, that is, a raffinate;

means for receiving a permeate, that is, the hydrogen separated by and discharged from the hydrogen separation reaction chamber of the fuel reformer, via a permeate header, controlling the pressure of the received permeate, and supplying the pressure-controlled permeate to an anode of a fuel cell;

means for controlling the pressure of the raffinate discharged from the hydrogen separation reaction chamber, thereby controlling the hydrogen separation reaction chamber of the fuel reformer; and valve means for supplying the raffinate to the combustion catalyst chamber of the fuel reformer.

FIG 1

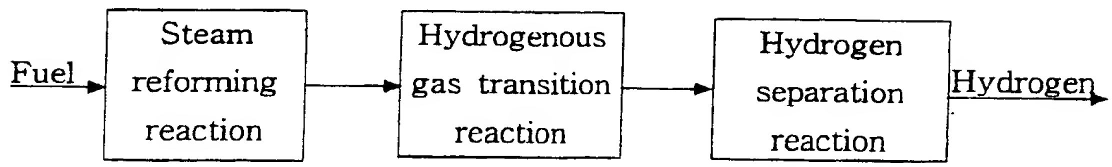

Fuel
Steam reforming reaction
Hydrogenous gas transition reaction
Hydrogen separation reaction
Hydrogen

FIG 2

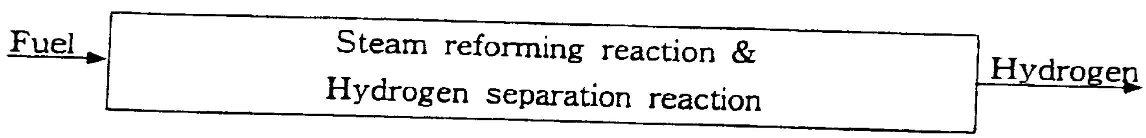

Fuel
Steam reforming reaction & Hydrogen separation reaction
Hydrogen

FIG 3

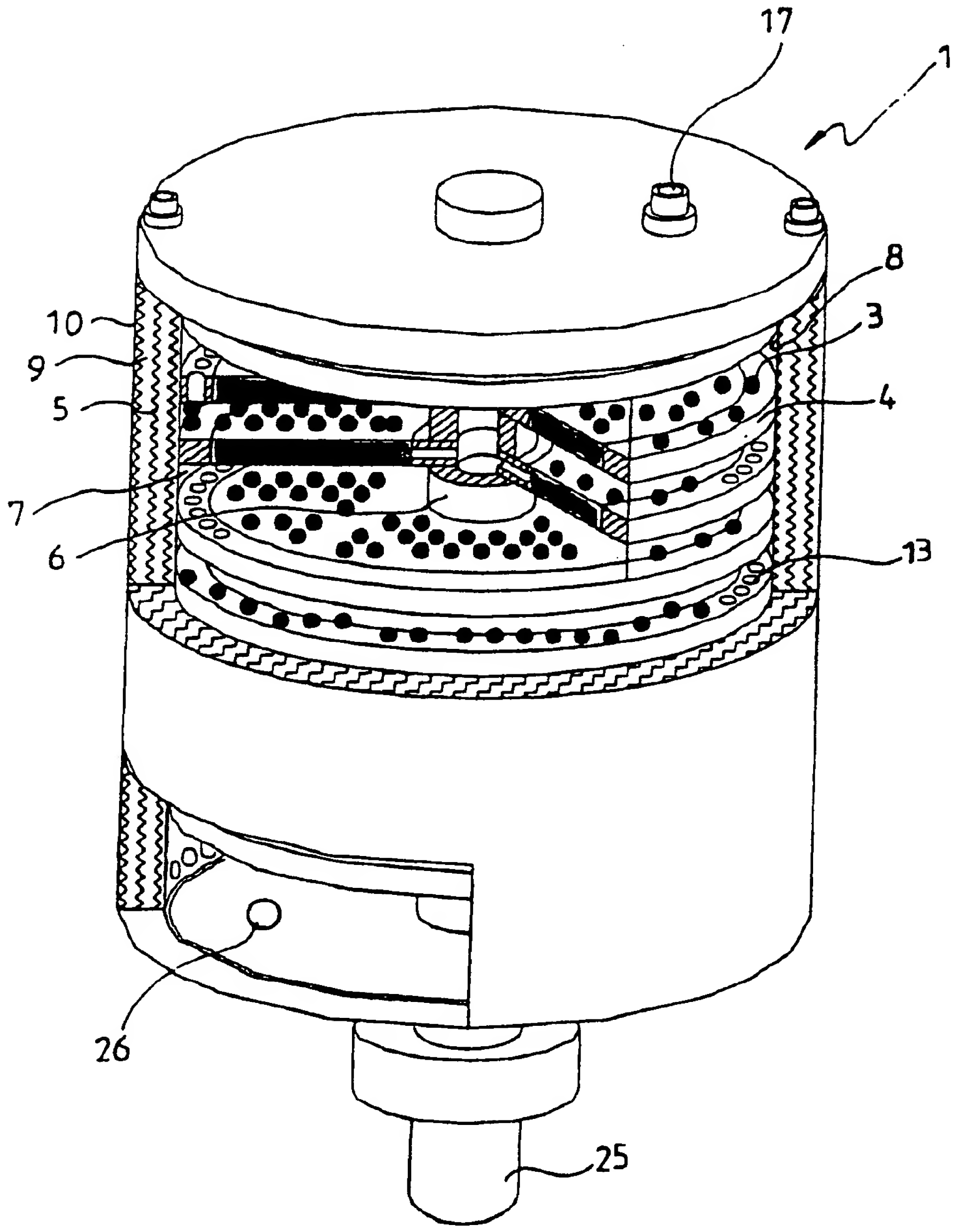


FIG 4

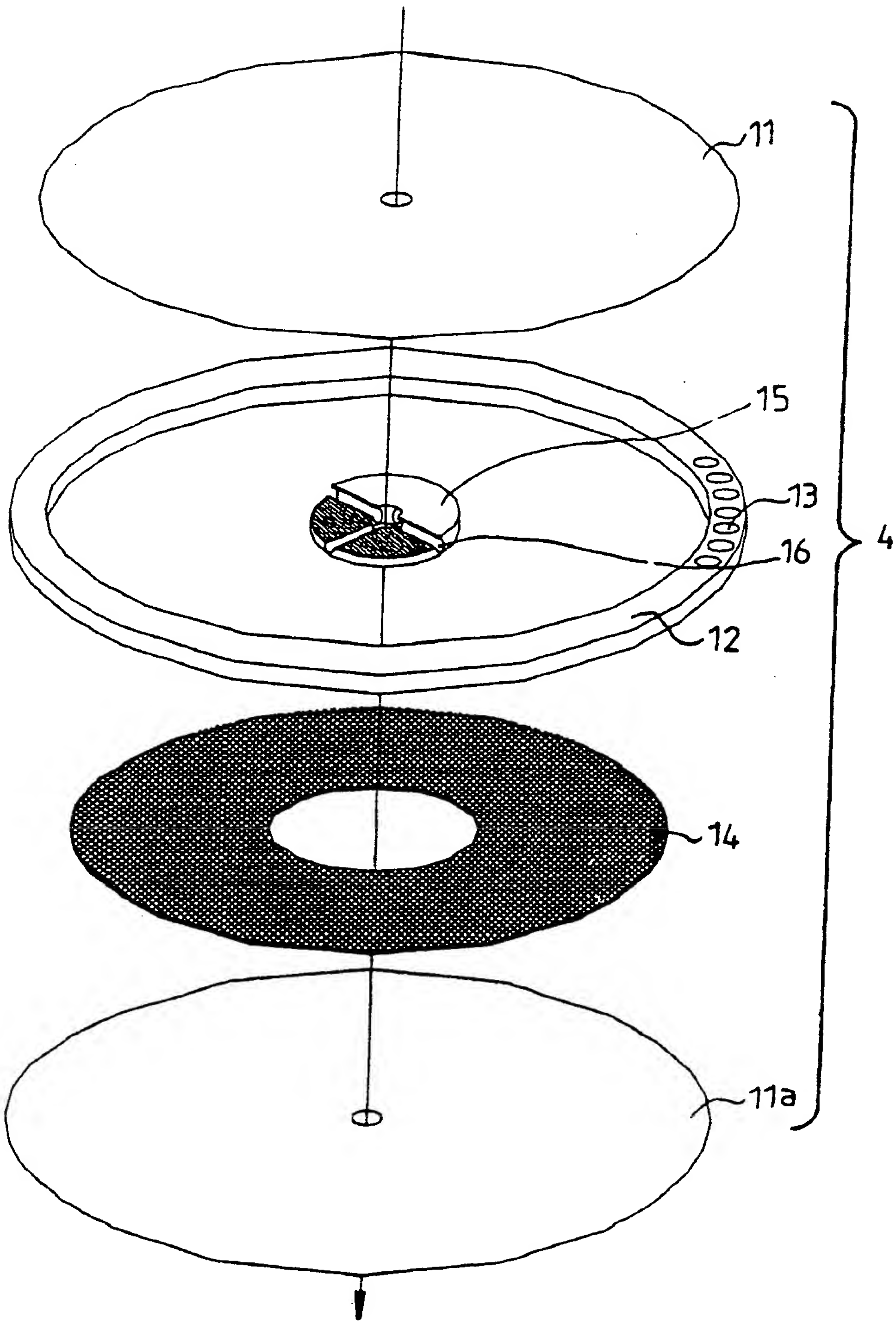


FIG 5

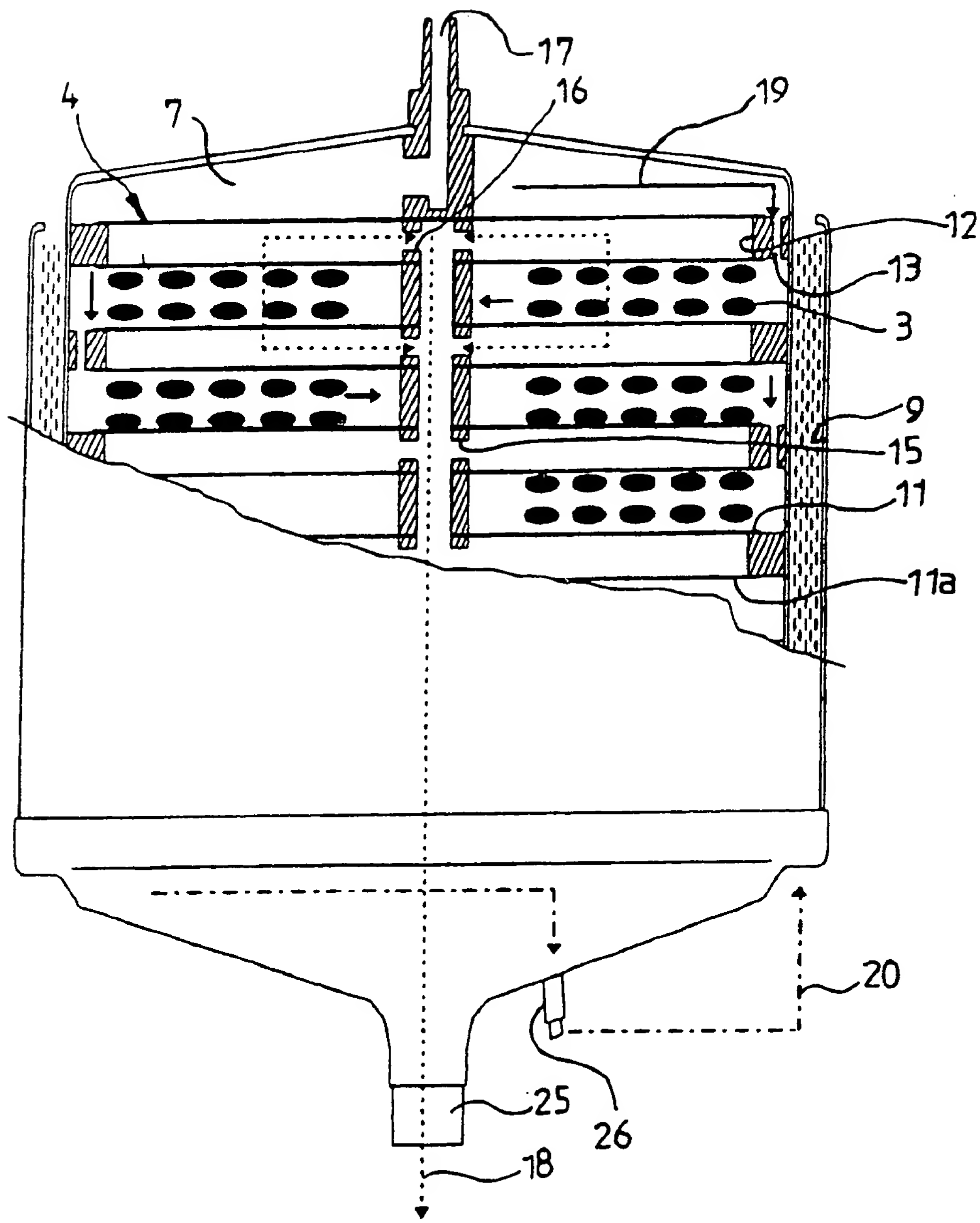


FIG 6

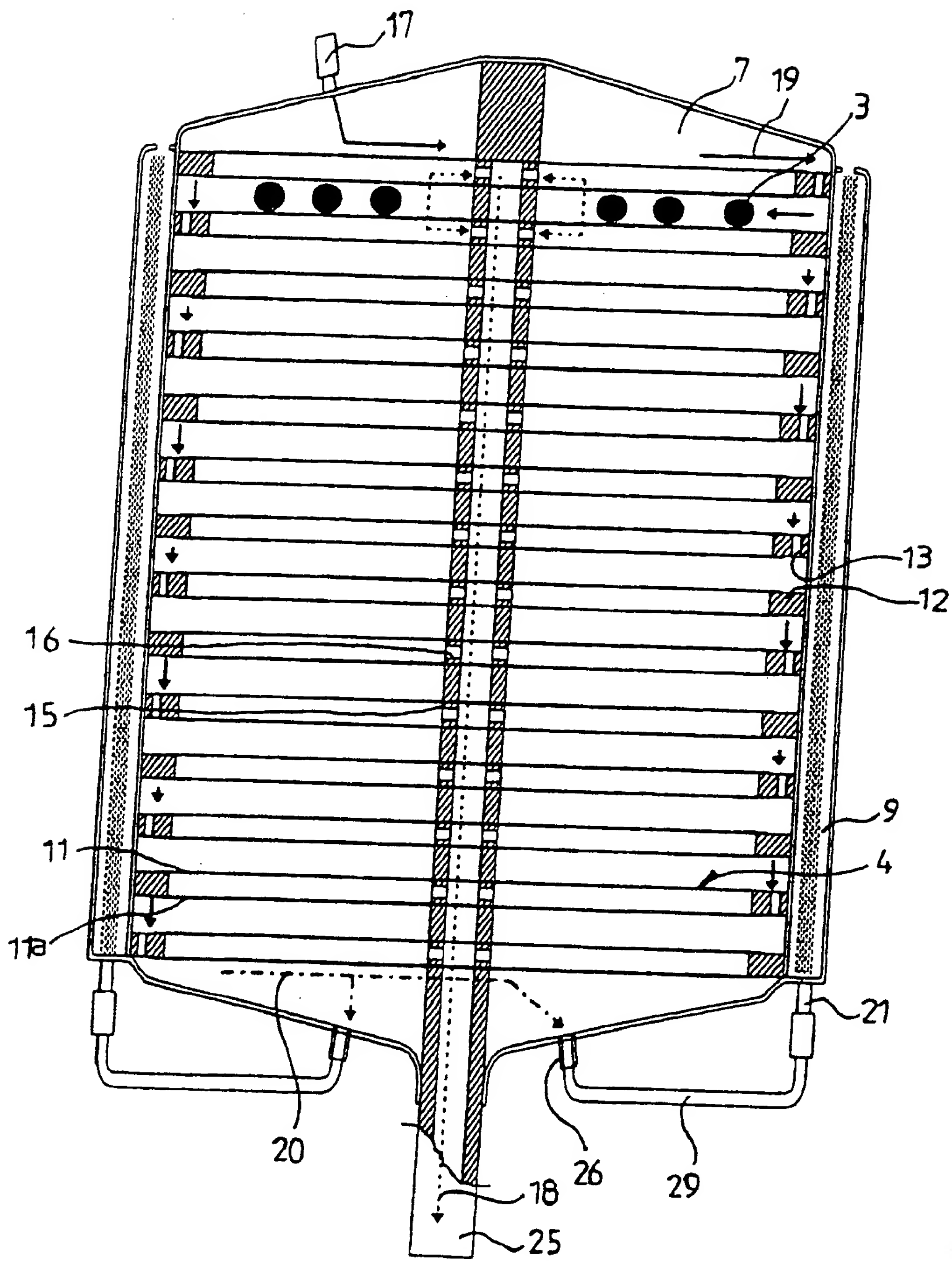
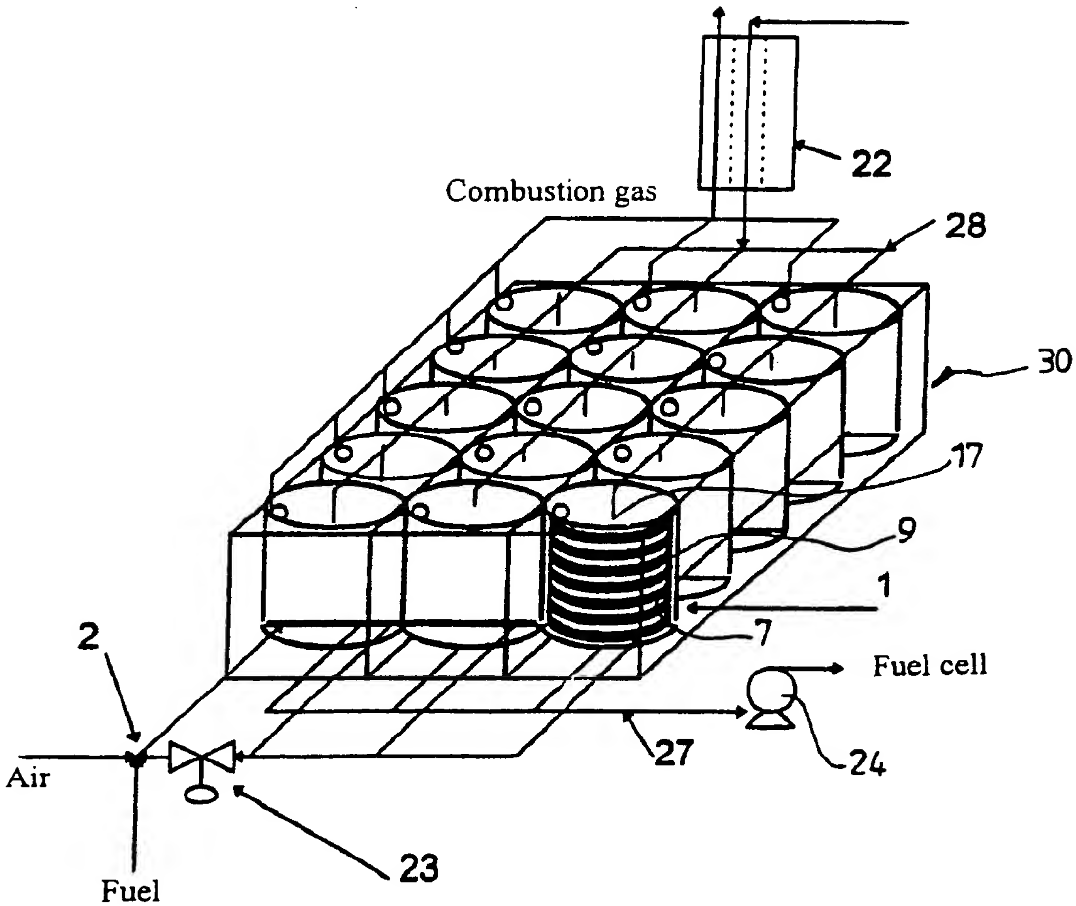


FIG 7



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 99/00524

A. CLASSIFICATION OF SUBJECT MATTER

IPC[7]: H 01 M 8/06; C 01 B 3/22, 3/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC[7]: H 01 M 8/00; C 01 B 3/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

AT, Chem. Abstr

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-WPI, Questel-CAS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0600621 A (Rolls Royce) 08 June 1994 (08.06.94) cited in the application.	1-8
A	WO 98/13125 A1 (Buxbaum) 02 April 1998 (02.04.98) cited in the application.	1-8
P,A	EP 0924162 A (DBB Fuel Cell) 23 June 1999 (23.06.99).	1-8
P,A	WO 99/19456 A (Northwest Power) 22 April 1999 (22.04.99).	1-8
P,A	US 5861137 A (Edmund) 19 January 1999 (19.01.99)	1-8
A	EP 0615949 A (Mitsubishi Heavy Ind) 21 September 1994 (21.09.94).	1-8
A	DE 19738513 A1 (DBB-Fuel Cell Engines) 05 November 1998 (05.11.98).	1-8

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
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„E" earlier application or patent but published on or after the international filing date
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„&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 November 1999 (11.11.99)	22 December 1999 (22.12.99)

Name and mailing adress of the ISA/AT	Authorized officer
Austrian Patent Office Kohlmarkt 8-10; A-1014 Vienna Facsimile No. 1/53424/200	Hammer Telephone No. 1/53424/374

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 99/00524

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 08-321321 A (TOKYO GAS CO et al) (abstract) 03 December 1996 (03.12.96). In: Patent Abstract of Japan [CD-ROM].	1-8
A	JP 06-168733 A (MITSUBISHI HEAVY IND Ltd) (abstract) 14 June 1994 (14.06.94). In: Patent Abstract of Japan [CD-ROM].	1-8
A	JP 05-155602 (SEKIYU SANGYO) Patent Abstracts of Japan, Vol. 17, Number 551 (C1117), 05 October 1993 (05.10.93) (abstract).	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR 99/00524

Patent document cited in search report			Publication date	Patent family member(s)			Publication date
EP	A1	600621	08-06-1994	CA	AA	2109655	03-06-1994
EP	B1	600621	16-04-1997	DE	C0	69309862	22-05-1997
				DE	T2	69309862	24-07-1997
				GB	A0	9225188	20-01-1993
				JP	A2	6239601	30-08-1994
				US	A	5458857	17-10-1995
WO	A1	9813125	02-04-1998	US	A	5888273	30-03-1999
EP	A2	924162	23-06-1999	DE	A1	19755813	01-07-1999
EP	A3	924162	20-10-1999	EP	A2	924161	23-06-1999
				EP	A3	924161	13-10-1999
				DE	A1	19757506	01-07-1999
WO	A1	9919456	22-04-1999	AU	A1	10849/99	03-05-1999
WO	C1	9919456	03-06-1999	EP	A1	951529	27-10-1999
US	A	5861137	19-01-1999			none	
EP	A2	615949	21-09-1994	CA	AA	2118956	17-09-1994
EP	A3	615949	09-11-1994	CA	C	2118956	25-08-1998
EP	B1	615949	15-09-1999	DE	C0	69420604	21-10-1999
				JP	A2	6263402	20-09-1994
				US	A	5639431	17-06-1997
				JP	A2	6263404	20-09-1994
				JP	A2	6263403	20-09-1994
				JP	A2	6263405	20-09-1994
				JP	A2	7109104	25-04-1995
				JP	A2	7109106	25-04-1995
				JP	A2	7109105	25-04-1995
DE	C1	19738513	05-11-1998	EP	A2	908536	14-04-1999
JP	A2	8321321	03-12-1996			none	
JP	A2	6168733	14-06-1994	JP	B2	2955040	04-10-1999
JP	A2	5155602	22-06-1993			none	